QUICK STUDY ACADEMIC

ORGANIC CHEMISTRY

FUNDAMENTALS

TYPES OF ORGANIC COMPOUNDS

HYDROCARBON

ALKANE C–H, C–C
- ethane: C_2H_6
- methyl (Me): $-CH_3$
- ethyl (Et): $-C_2H_5$

ALKENE >C=C<
- ethene: C_2H_4
- diene: two C=C
- triene: three C=C

ALKYNE $-C\equiv C-$
- ethyne: C_2H_2

AROMATIC
- benzene: C_6H_6
- arene: C_6H_5 (Ar-)

-O- ADDED

ALCOHOL R–O–H
- methanol: Me-OH (methyl alcohol)
- phenol: Ar-OH
- diol/glycol: (2 -OH)
- glycerol: (3 -OH)

ETHER R–O–R
- ethoxyethane: Et-O-Et (diethyl ether)

EPOXY
- cyclic ether

PEROXIDE R-O-O-R'

>C =O ADDED

ALDEHYDE
- methanal: H_2CO (formaldehyde)
- benzaldehyde: Ar-CHO

KETONE
- 2-propanone: Me-CO-Me (dimethyl ketone, acetone)
- diketone: R-CO-R"-CO-R'

>COO ADDED

CARBOXYLIC ACID
- ethanoic acid: Me-COOH (acetic acid)
- acetate ion: $Me-COO^-$
- benzoic acid: Ar-COOH

Dicarboxylic acid HOOC-R-COOH

ESTER
- ethyl acetate: Me-CO-OEth,

Other derivatives:
- Peroxyacid: R-CO-OOH
- Acid anhydride: RCO-O-CO-R'

NITROGEN ADDED

AMINE
- methyl amine: H_3C-NH_2
- phenylamine: $Ar-NH_2$ (aniline)
- $R-NH_2$ (1°), RR'NH (2°), RR'R"N (3°)

NITRO $R-NO_2$

DIAZO $R-N\equiv N$

NITRILE $R-C\equiv N$
- methane nitrile: Me-CN

AMIDE
- acetamide: $Me-CO-NH_2$

SULFUR ADDED

- thiol: R-SH
- thioether: R-S-R'
- disulfide: R-S-S-R'
- thiol ester: R-CO-SR'
- sulfoxide: R-SO-R'
- sulfone: $R-SO_2-R'$
- sulfonic acid: $R-SO_3H$

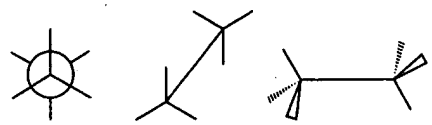
HALOGEN ADDED
- haloalkane: R–X Me-Cl chloromethane
- halobenzene: Ar-X chlorobenzene: Ar-Cl
- acyl halide: R-CO-X
- aryl halide: Ar-X

FORMULAS AND ISOMERS

Molecular formula: elemental symbols with subscripts denote the composition of a compound

Empirical formula: subscripts denote the relative elemental composition

Graphical depiction:
- Dash formula: diagram all atoms, bonds as dashes
- Bond line formula: hide H, show carbon skeleton as lines, other atoms explicit



Newman projection formula

Sawhorse formula

- Newman Projection: 2-d depiction
- 3-dimensional: wedges of sawhorse denote structure

SUBDIVISIONS OF ISOMERS

Isomers
Different compounds with same molecular formula

- **Constitutional isomers**: Atoms have a different connectivity
- **Stereoisomers**: Same connectivity - differ in the arrangement of their atoms in space
  - **Enantiomers**: Stereoisomers that are nonsuperimposable mirror images of each other
  - **Diastereomers**: Stereoisomers that are not mirror images of each other

constitutional isomers: different bonding connectivity (ex. rings, bonds, branching, substituent positions)

tautomers: easily interconverted structural isomers (ex. keto-enol for ketone)

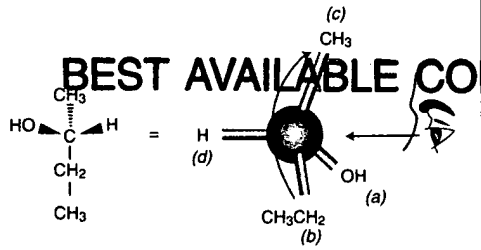
chiral: not identical with mirror image

achiral: has plane of symmetry (superimposable on mirror-image)

epimers: a pair of diastereomers which differ only in the configuration of one atom

More than 1 chiral center:
- n chiral centers, $\leq 2^n$ stereoisomers
- **meso**: two chiral centers, 4 isomers: 3 stereoisomers, 1 achiral (mirror-plane)

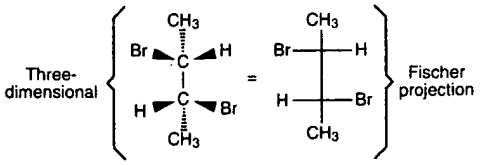
FORMULAS AND ISOMERS



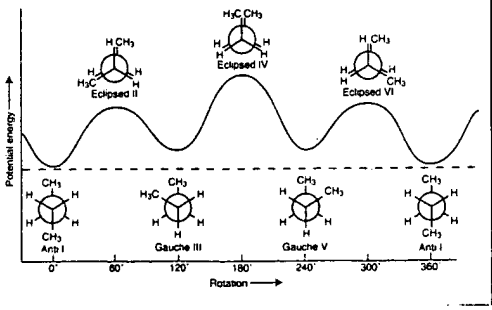
Arrows are clockwise

R/S notation: the four different atoms or groups attached to a central atom are ranked a,b,c,d, by molar mass. The lowest (d) is directed away from the viewer and the sequence of a-b-c produces clockwise (R) or counter-clockwise (S) configuration.
- **chiral (optically active)**: + or – rotation of plane polarized light. R/S: opposite effects
- **racemic**: 50/50 mixture of stereoisomers (no net optical activity)
- **nomenclature**: note R/S and +/- in the compound name; example: R (+) bromochloromethanol.

Fisher-projection: diagram depicts chiral/3-D structure
- **molecular conformations**: molecule exhibits structural variation due to free rotation about C-C single bond



Newman-diagram: depict rotation about a C-C bond; **eclipsed** (high energy), **anti** (low energy), **gauche** (intermediate energy)



COMMON TERMS

aliphatic: non-aromatic
aromatic: benzene ring
heterocyclic: non-carbon atom in the ring structure
hydrocarbon: compound of H and C
paraffin: alkane
olefin: alkene
saturated: maximum # of H's (all C-C single bonds)
unsaturated: at least one C-C multiple bond

NOMENCLATURE

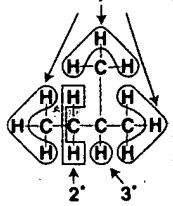
IUPAC - standard guidelines for naming compounds
Nomenclature Strategy - find longest carbon chain, identify and note location of functional groups and substituents by chain position number.
Classes of compounds are defined by the functional group. There are many common names and functional group names. Multiple names are possible.

CARBON CHAIN PREFIXES

# of C's	Prefix	R-group
1	meth-	methyl
2	eth-	ethyl
3	prop-	propyl
4	but-	butyl
5	pent-	pentyl
6	hex-	hexyl
7	hept-	heptyl
8	oct-	octyl
9	non-	nonyl
10	dec-	decyl

cyclo-: ring structure; example: cyclopropane 3-carbon ring molecule
iso-: two methyl groups on the terminus of a chain
n-: normal straight chain
t-: tertiary alkyl group
vic (vicinal): two substituents on adjacent carbons
gem (geminal): two substituents on the same carbon
alkene isomers: cis or trans
benzene substitution positions: ortho(1,2), meta (1,3), para (1,4)

Carbon atoms & associated H-atoms



Carbon Position

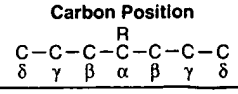
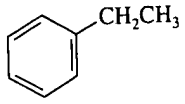
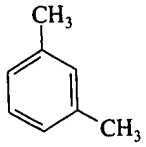
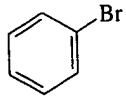
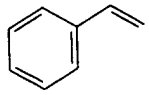


TABLE 16-2 Ultraviolet Spectra of Benzene and Some Derivatives

Compound	Structure	Moderate Band λ_{max}(nm)	Moderate Band ε	Benzenoid Band λ_{max}(nm)	Benzenoid Band ε
benzene		204	8,800	254	250
ethylbenzene		208	7,800	260	220
m-xylene		212	7,300	264	300
bromobenzene		210	7,500	258	170
styrene		248	15,000	282	740

5 nm, as shown by the examples in Table 16-2. An additional conjugated double bond can increase the value of λ_{max} by about 30 nm, as shown by the UV spectrum of styrene in Figure 16-17.

PROBLEM 16-23

The UV spectrum of 1-phenyl-2-propen-1-ol shows an intense absorption at 220 nm and a weaker absorption at 258 nm. When this compound is treated with dilute sulfuric acid, it rearranges to an isomer with an intense absorption at 250 nm and a weaker absorption at 290 nm. Suggest a structure for the isomeric product and give a mechanism for its formation.

Chapter 16 Glossary

aliphatic compound An organic compound that is not aromatic. (p. 690)

annulenes Cyclic hydrocarbons with alternating single and double bonds. (p. 694)

[6]annulene (benzene) [10]annulene (cyclodecapentaene)

aromatic compound A cyclic compound containing some number of conjugated double bonds, characterized by an unusually large resonance energy. (pp. 691, 700)

To be aromatic, all its ring atoms must have unhybridized *p* orbitals that overlap to form a continuous ring. In most cases, the structure must be planar and have $(4N + 2)$ pi electrons, with N an integer. Delocalization of the pi electrons over the ring results in a lowering of the electronic energy.

antiaromatic compound A compound that has a continuous ring of *p* orbitals as in an aromatic compound, but delocalization of the pi electrons over the ring increases the electronic energy. (p. 700)

In most cases, the structure must be planar and have $(4N)$ pi electrons, with N an integer.

arenes Aromatic hydrocarbons, usually based on the benzene ring as a structural unit. (p. 715)

aryl group (abbreviated Ar) The aromatic group that remains after taking a hydrogen atom off an aromatic ring; the aromatic equivalent of the generic alkyl group (R). (p. 718)

benzenoid band The weak band around 250 to 270 nm in the UV spectra of benzenoid aromatics. This band is characterized by multiple sharp absorptions (fine structure). (p. 721)

benzyl group ($PhCH_2$—) The seven-carbon unit consisting of a benzene ring and a methylene group. (p. 718)

degenerate orbitals Orbitals having the same energy. (p. 696)

fused rings Rings that share a common carbon–carbon bond and its two carbon atoms. (p. 713)

heterocyclic compound (heterocycle) A cyclic compound in which one or more of the ring atoms is not carbon. (p. 709)

aromatic heterocycle: a heterocyclic compound that fulfills the criteria for aromaticity and has a substantial resonance energy.

Hückel's rule A cyclic molecule or ion that has a continuous ring of overlapping *p* orbitals will be

1. aromatic if the number of pi electrons is $(4N + 2)$, with N an integer.
2. antiaromatic if the number of pi electrons is $(4N)$, with N an integer. (p. 701)

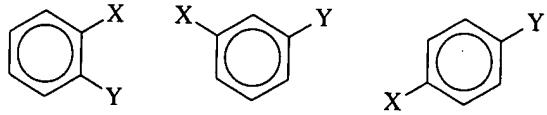
Kekulé structure A classic structural formula for an aromatic compound, showing localized double bonds. (p. 690)

nonaromatic compound Neither aromatic nor antiaromatic; lacking the continuous ring of overlapping *p* orbitals required for aromaticity or antiaromaticity. (p. 700)

ortho Having a 1,2-relationship on a benzene ring. (p. 716)

meta Having a 1,3-relationship on a benzene ring. (p. 716)

para Having a 1,4-relationship on a benzene ring. (p. 716)

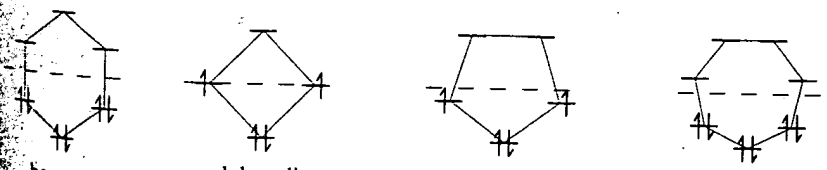


ortho (1,2) meta (1,3) para (1,4)

phenyl group (Ph or ϕ) The benzene ring, minus one hydrogen atom, when named as a substituent on another molecule. (p. 717)

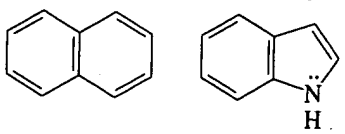
polygon rule The energy diagram of the MOs of a regular, completely conjugated cyclic system has the same polygonal shape as the compound, with one vertex (the all-bonding MO) at the bottom. The nonbonding line cuts horizontally through the center of the polygon. (p. 699)

Energy diagrams



benzene cyclobutadiene cyclopentadienyl cation tropylium ion

polynuclear aromatic compounds Aromatic compounds with two or more fused aromatic rings. Naphthalene is an example of a **polynuclear aromatic hydrocarbon** (PAH or PNA), and indole is an example of a polynuclear aromatic heterocycle. (p. 713)



naphthalene indole

resonance energy The extra stabilization provided by delocalization, compared with a localized structure. For aromatic compounds, the resonance energy is the extra stabilization provided by the delocalization of the electrons in the aromatic ring. (p. 693)

tropylium ion The cycloheptatrienyl cation. (p. 707)